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Mutual Solubility of MEG, Water and Reservoir Fluid: Experimental Measurements and Modeling using the CPA Equation of State

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Abstract

This work presents new experimental phase equilibrium data of binary MEG-reservoir fluid and ternary MEG-water-reservoir fluid systems at temperatures 275-326 K and at atmospheric pressure. The reservoir fluid consists of a natural gas condensate from a Statoil operated gas field in the North Sea.

Prediction of mutual solubility of water, MEG and hydrocarbon fluids is important for the oil industry to ensure production and processing as well as to satisfy environmental regulations. The CPA equation of state has been successfully applied in the past to well defined systems containing associating compounds. It has also been extended to reservoir fluids in presence of water and polar chemicals using a Pedersen like characterization method with modified correlations for critical temperature, pressure and acentric factor. In this work CPA is applied to the prediction of mutual solubility of reservoir fluid and polar compounds such as water and MEG. Satisfactory results are obtained for mutual solubility of MEG and gas condensate whereas some deviations are observed for the ternary system of MEG-water-gas condensate.

1. Introduction

As the exploitable oil resources decrease, more sophisticated recovery methods are employed in the oil industry to produce the remaining resources. One result of using more sophisticated recovery methods is that oil field chemicals are more widely used, especially in the offshore oil production. These chemicals belong to different families like alcohols, glycols, alkanolamines, surfactants and polymers. They have various functions, e.g., methanol and MEG are used as gas hydrate inhibitors, surfactants are used to lower interfacial tension between crude oil and microemulsion and polymers in a polymer-waterflooding process act primarily as thickeners. Over the last years, the use of these chemicals has increased considerably [1, 2].

The knowledge of the phase equilibria of aqueous mixtures with hydrocarbons and chemicals is important for environmental purposes since hydrocarbons must be removed from gas processing, refinery and petrochemical plant wastewater streams and from sea or fresh water when oil spills occurs. For this purpose, the solubility and volatility of hydrocarbons is required to describe their phase distribution through the removal process. Such information is also important in the design and operation of separation equipments. In addition, it is also useful in predicting the water and the chemical contents of the fuels [3].

The cubic equations of state play an important role in chemical engineering design, and they have assumed an expanding role in the study of the phase equilibria of fluids and fluid mixtures [4]. Most phase equilibrium calculations on oil and gas mixtures are performed using a cubic equation of state, for example, the Soave-Redlich-Kwong (SRK) or Peng-Robinson (PR) EoS [5]. However, systems containing reservoir fluids and polar/associating compounds (e.g. water, glycols and methanol etc.) are hard to describe using the conventional EoS especially at high temperature and pressure conditions [6]. The CPA equation of state has been very successful in describing such complex systems [7].

The CPA equation of state (EoS), proposed by Kontogeorgis et al. [8], is an extension of the conventional SRK EoS. The equation combines the simplicity of a cubic equation of state and Wertheim's theory for the association part [4]. It gives a better description of systems containing associating compounds compared with the empirical or semi-empirical modifications of cubic EoS, and reduces to the SRK EoS for non-associating compounds [6]. In previous studies CPA has been extensively tested for well-defined systems containing associating compounds, most of which have already been summarized by Kontogeorgis et al. [9, 10, 7].

The CPA EoS has been extended to reservoir fluids by Yan et al. [6] using a characterization procedure similar to that of Pedersen et al. [11] and a set of new correlations for the critical properties for CPA. Calculations presented for reservoir fluids-water and reservoir fluids/water/methanol glycols showed promising results. However, data are available for very few systems, especially gas condensates, and more data are required for an extensive investigation and full validation of the model [7].

In this work new experimental data for the mutual solubility of gas condensate-MEG and gas condensate-MEG-water systems are presented. Thermodynamic modeling for mutual solubility of the above systems is also carried out using the CPA EoS and the characterization method of Yan et al. [6]. The paper is divided into two sections: the first section about the experimental work and the second section about the thermodynamic modeling. The experimental section presents the experimental setup, the experimental

procedure, the analysis method and the experimental results. The modeling section briefly describes the CPA EoS and the characterization method, and discusses the modeling results obtained with the CPA.

2. Experimental Section

2.1. Materials

The chemicals used in this work are shown in Table 1 and no further purification was carried out.

2.2. Apparatus and Procedure

The sketch for the experimental setup used in this work is shown in Figure 1. A similar setup has been used in the previous work by Folas et al. [12] and Derawi et al. [13] for experimental study of liquid-liquid equilibria of well defined hydrocarbons and polar compounds. In this work some necessary modifications were made in analysis methods because hydrocarbon phase is a reservoir fluid of higher complexity as compared to well defined hydrocarbons.

2.2.1. Mixing and Equilibrium

MEG, gas condensate and water were mixed at a fixed temperature for 24 hours using a mixing machine in an air heated oven. For binary systems, approximately equal mass of MEG and condensate were added for mixing. The ternary system consists of MEG, condensate and water where the hydrocarbon phase was 50% (mass) and the polar phase was also 50% on mass basis. The polar phase consists of MEG and water where the composition of MEG ranges from 40% to 90% which is of interest to the industrial applications in the North Sea.

After mixing the mixture was transferred to two identical glass equilibrium cylinders and was kept for at least 18 hours to attain equilibrium. The equilibrium cylinders contain holes and caps fitted with septa for sampling. Both mixing and separation were carried out in an air heated oven which was used at the temperature range from 275 K to 326 K in this work. A DOSTMANN P500 thermometer ($\pm 0.1\ ^{o}C$) was used for the temperature measurement.

2.2.2. Sampling and Analysis

At equilibrium, samples from two phases were drawn manually using a preheated syringe and needle. Preheated needle was used to avoid phase separation due to temperature gradient. Two Agilent gas chromatographs (GCs) with different column specifications were used for composition analysis: one for the polar phase (glycol GC) while another for the condensate phase (condensate GC). The characteristics of gas chromatographs used in this work are given in Table 2. The gas chromatographs are connected to a computer which has Chem Station package for data acquisition and quantification.

Polar Phase Analysis for the Solubility of Gas Condensate in MEG

For the polar phase analysis, hydrocarbons were extracted using solvent extraction method. The solvent used in this work for the extraction of hydrocarbons from the polar phase is carbon disulphide (CS_2) which has negligible solubility in MEG but it is soluble in hydrocarbons. The extract phase is then analyzed on condensate GC using the standard temperature program from ASTM standard D5134-98 [14] with an internal standard 1-heptene diluted in 1-dodecane (C_{12}). The authors are aware of the fact that the original method "ASTM D5134" does not use any internal standard. But quantification of dissolved condensate in polar phase becomes easier with an internal standard. The internal standard method also accounts for any variances in the gas chromatograph performance. The analyte chosen for the internal standard has a predictable retention time and area, allowing it to be used to determine if abnormalities have occurred.

Condensate Phase Analysis for Solubility of the MEG in Gas Condensate

MEG dissolved in condensate was extracted using water and analyzed at GC1. The water contents of condensate phase were analyzed using Karl Fisher Coulometer which provides very fast and reliable results, especially for systems with very low solubilities.

2.3. Experimental Results

The experimental work was initiated with the well defined system of MEG with n-heptane and a similar procedure was adopted as in a previous work [12, 13]. The experimental results from this work are given in Figure 2 in comparison with the experimental data from the literature. The solubility data of n-heptane in MEG is in good agreement with those of Stavely et al. [16], Derawi et al. [17] and Lindboe et al. [18]. On the other hand solubility data of MEG in n-heptane is in good agreement with the data from Lindboe et al. whereas slightly lower than those from Stavely et al. and Derawi et al.

The composition of gas condensate (COND-1) used in this study is given in Table 3 with additional information on molecular weight and density of condensate and its different carbon fractions. The overall density and molecular weight of COND-1 have been measured experimentally, whereas the density and molecular weight of other components given in Table 3 are either calculated or literature values. The mutual solubility data for the binary mixture (MEG, COND-1) are presented in Table 4 and for the ternary mixture (MEG, Water, COND-1) in Table 5 (mole fraction).

The experimental data were measured in mass fraction. In order to compare with the modeling results, it is required to convert them into molar composition. Here we need the average molecular weight of the condensate dissolved in the polar phase which is different from the molecular weight of the original condensate in the feed. This is because the components in the original condensate will partition in different

ratios between the condensate phase and the polar phase. The average molecular weight M of the dissolved condensate in the polar phase was calculated by equation 1:

$$M = \sum_{i=1}^{i=n} x_i M_i \qquad 1$$

where x_i is the normalized mole fraction of component i in the condensate dissolved in polar phase and M_i is the molecular weight of component i.

A gas condensate and an oil will typically contain paraffinic (P) naphthenic (N) and aromatic (A) compounds. The solubility of MEG in a specific carbon fraction (e.g. C_7) will be the highest in the aromatic HC (e.g. benzene) and the lowest in the paraffinic HC (e.g. n-heptane). The same is also true for the solubility of HC in MEG. As a gas condensate contains both paraffinic and aromatic hydrocarbons, it is expected that the solubility of MEG in condensate should lie between the solubility of MEG in benzene and the solubility of MEG in n-heptane. This is illustrated in Figures 3 and 4 where it is shown that the solubility of MEG and condensate lie between the values for the solubilities in the aromatic C_7 (benzene) and the paraffinic C_7 (n-C_7).

3. Thermodynamic modeling

3.1. The CPA Equation of State

The CPA equation of state (EoS), proposed by Kontogeorgis et al. [8], is an extension of the conventional SRK EoS. It can be expressed as a sum of the SRK EoS and the contribution of association term as given by equation 2.

$$P = \frac{RT}{V_m - b} - \frac{\alpha(T)}{V_m(V_m + b)} - \frac{1}{2}\frac{RT}{V_m}\left(1 + \frac{1}{V_m}\frac{\partial \ln g}{\partial(1/V_m)}\right)\sum_i x_i \sum_{A_i}(1 - X_{A_i}) \qquad 2$$

The first two terms on the right-hand side are the same as in the SRK EoS, while the last term is the one that accounts for association. The last association term is therefore eliminated if inert (non-associating) compounds like hydrocarbons are present.

In the association part X_{A_i} is the mole fraction of the molecule i not bonded at site A and x_i is the mole fraction of component i.

X_{A_i} is given by the following equation:

$$X_{A_i} = \frac{1}{1+\frac{1}{V_m}\sum_j x_j \sum_{B_j} X_{B_j} \Delta^{A_i B_j}} \quad (3)$$

where $\Delta^{A_i B_j}$ is the association strength between site A on molecule i and site B on molecule j and is given by:

$$\Delta^{A_i B_j} = g(V_m)^{ref} \left[\exp\left(\frac{\varepsilon^{A_i B_j}}{RT} \right) - 1 \right] b_{ij} \beta^{A_i B_j} \quad (4)$$

with the radial distribution function $g(\rho) = 1/(1-1.9\eta)$ where $\eta = (1/4) b\rho$.

The parameters $\varepsilon^{A_i B_j}$ and $\beta^{A_i B_j}$ are the association energy and volume between site A of molecule i and site B of molecule j, respectively.

The energy parameter in the SRK part of the equation is given by a Soave-type temperature dependency, whereas b is temperature independent:

$$a(T) = a_0[1 + c_1(1 - \sqrt{T/T_c})]^2 \quad (5)$$

3.1.1. Mixing and combining rules

The CPA EoS when applied to mixtures requires mixing rules only for the SRK part, while the association part is extended to mixtures in a straightforward way. The classical van der Waals one-fluid mixing rules are used for a and b:

$$a = \sum_i \sum_j x_i x_j a_{ij} \quad (6)$$

$$b = \sum_i \sum_j x_i x_j b_{ij} \quad (7)$$

where a_{ij} and b_{ij} are calculated by the following combining rules:

$$a_{ij} = \sqrt{a_i a_j}(1 - k_{ij}) \quad (8)$$

$$b_{ij} = \frac{b_i + b_j}{2} \quad (9)$$

where k_{ij} is a binary interaction parameter which is fitted to experimental data.

For mixtures containing more than one associating compounds such as the mixture of glycols and water, combining rules are needed for the association parameters. Different combining rules have been suggested, but in this work only the Elliott Combining Rule (ECR) is used as given in equation 10:

$$\Delta^{A_iB_j} = \sqrt{\Delta^{A_iB_i}\Delta^{A_jB_j}} \qquad 10$$

The ECR can satisfactorily describe the water-MEG system of relevance to this work.

The pure component parameters a_0, b and c_1 in the SRK part are obtained by fitting vapor pressure and saturated liquid density data rather than from the critical point constraints. Therefore, they cannot be calculated directly from the experimental critical temperature (T_c), critical pressure (P_c), and acentric factor (ω). Instead, those three parameters correspond to a set of apparent critical temperature, pressure and acentric factor. The subscript m is used to indicate that they are the CPA "monomer" parameters rather than the experimental values. The following equations were used by Yan et al. [6] to calculate T_{cm}, P_{cm} and m_m from a_0, b and c_1:

$$m_m = c_1\sqrt{\frac{a_0\Omega_B}{bRT_c\Omega_A}} \qquad 11$$

$$T_{cm} = T_c\left(\frac{1+1/c_1}{1+1/m_m}\right)^2 \qquad 12$$

$$P_{cm} = \frac{\Omega_B RT_{cm}}{b} \qquad 13$$

where $\Omega_A = 0.42748$, $\Omega_B = 0.08664$ and

$$m_m = 0.480 + 1.574\ \omega_m - 0.176\ \omega_m^2 \qquad 14$$

The pure component parameters for polar compounds and the association schemes used in the calculations are given in Table 6.

The hydrocarbon fractions that constitute the condensate cover a wide range from light to heavy carbon fractions and therefore different k_{ij} for each pair (of MEG-HC) should be used. The k_{ij} usually comes from well defined systems (e.g. MEG-hexane, MEG-heptane etc.). The MEG-HC systems previously studied using the CPA EoS are given in Table 7 along with the interaction parameters used.

It can be seen from Table 7 that the interaction parameters are available for few HC (paraffinic and naphthenic) components and MEG due to scarcity of experimental data and possible difficulty involved in measurement of such low solubilities. The condensate involved in this study does not contain any methane therefore the interaction parameters that can be used from Table 7 are only of heptane, hexane and methylcyclohexane with MEG. In this work a simple approach is adopted i.e. to use the same k_{ij} for all MEG-HC pairs. The k_{ij} used are temperature independent.

The binary interaction parameters between water and hydrocarbons are obtained from a generalized expression using the equation given in Table 8 [24] which presents % AAD in the solubility of water in the hydrocarbon as well as the solubility of HC in the aqueous phase for various water-alkane systems.

As Table 8 presents, the water solubility in the HC phase can be satisfactorily correlated using generalized correlation expression. The overall correlation of the hydrocarbon solubility in the aqueous phase is slightly inferior (but still adequate compared to various SAFT-variants), mainly due to the minimum in the solubility at low temperature which cannot be described using CPA. However the performance of the model at elevated temperatures is satisfactory [24].

3.2. Heptanes plus characterization

To perform phase equilibrium calculations for a reservoir fluid using cubic equations of state, the critical temperature (T_c), the critical pressure (P_c), and the acentric factor (ω) are required for each component contained in the mixture. In addition, a binary interaction parameter (k_{ij}) may also be needed for each pair of components. Naturally occurring oil or gas condensate mixtures may contain thousands of different components. Such high numbers are impractical to handle in phase equilibrium calculations. Some components therefore must be lumped together and represented as pseudocomponents. C_{7+} characterization consists of representing the hydrocarbons with seven and more carbon atoms (the heptane plus or C_{7+} fraction) as a convenient number of pseudo components and finding the necessary EoS parameters (T_c, P_c and ω) for each of the pseudo components [25].

To characterize C_{7+} fraction in reservoir fluids, two methods are often used: the method proposed by Pedersen et al. [11, 26] and that by Whitson et al. [27]. Both methods share three common steps:

i. Determination of the detailed molar composition in the C_{7+} fraction
ii. Estimation of EoS parameters (T_c, P_c, ω)
iii. Lumping of detailed C_{7+} fractions into a few pseudo components

Yan et al. proposed modified correlations for the second step and details of the development can be found elsewhere [6, 7]. A two step perturbation method is used in order to develop correlations for modified critical temperature (T_{cm}), critical pressure (P_{cm}) and acentric factor (ω_m) to use for CPA. Perturbation expansion correlations were developed by Twu [28], which initially correlate the properties of normal paraffins as the reference, and then extend these correlations to petroleum fractions:

$$T_{cm0} = \frac{(1885.45947 + 0.222337924T_b)T_b}{950.853406 + T_b} \quad (15)$$

$$\ln P_{cm0} = -4.05282558\times10^{-12}T_b^{\,4} + 8.76125776\times10^{-9}T_b^{\,3} - 7.4578304\times10^{-6}T_b^{\,2} - 1.09972989\times10^{-4}T_b + 4.16059295 \quad (16)$$

$$\omega_{m0} = \exp\left(\frac{-2553.0653 + 3.68418T_b}{608.7226 + T_b}\right) \quad (17)$$

In the above equations, T_b and T_{cm0} are in Kelvin, and P_{cm0} is in bar. The subscript 0 refers to the properties of n-alkanes. Soave's correlation [29] is used to calculate the specific gravity for n-alkanes:

$$SG_0 = (1.8T_b)^{1/3}(11.7372 + 3.336\times10^{-3}T_b - 976.3T_b^{-1} + 3.257\times10^{5}T_b^{-2})^{-1} \quad (18)$$

For the perturbation step, ΔSG is used to account for the aromaticity of the fraction. Aromatic compounds generally have higher densities than normal alkanes at the same T_b. And as a general trend, the larger ΔSG is, the higher are the differences between T_{cm} and T_{cm0}, and between P_{cm} and P_{cm0}. The final equations proposed by Yan et al. [6] are:

$$T_{cm}/T_{cm0} = (1\text{-}12.0690795\Delta SG + 22.8626562\Delta SG^2 + 89.7115818\Delta SG^3)/(1\text{-}12.6311386\Delta SG + 30.6779472\Delta SG^2 + 62.4698965\Delta SG^3) \quad (19)$$

$$\ln(P_{cm}/P_{cm0}) = \Delta SG[\text{-}677.989269 + (76624.406 - 29811.8749/SG)\Delta SG]/(1+10949.2202\Delta SG + 28099.1573\Delta SG^2) \quad (20)$$

The CPA acentric factor ω_m is not treated as a free parameter. Instead, it is back calculated by matching the T_b of the fraction. The direct vapor pressure calculation procedure proposed by Soave [26] can be used which does not need any iteration. Equation 17 is used only if T_b exceeds T_c for very heavy compounds.

The detailed composition of COND-1 is given in Table 3 . By using information from Table 3 and Pedersen et al. [11] method of characterization with the modified correlation of Yan et al. [6] for critical temperature, critical pressure and acentric factor, the COND-1 has been characterized and the results (T_{cm}, P_{cm}, ω_m etc.) obtained after lumping are given in Table 9.

3.3. Results and Discussion

3.3.1. Solubility of MEG and n-Heptane

The modeling results for MEG and n-heptane are given in Figure 5 in comparison to experimental data from literature. The binary interaction parameter between n-heptane and MEG ($k_{ij} = 0.047$) as given in Table 7 is taken from Derawi et al. [23].

CPA can satisfactorily describe mutual solubility of MEG and n-heptane especially in temperature range of 316-352 K as shown in Figure 5. At lower temperatures the solubility of MEG in n-heptane is over estimated whereas the solubility of n-heptane in MEG is under estimated. This may be due to the fact that CPA cannot describe the (minimum in) solubility at low temperature. But it has been reported that modeling results are still adequate in comparison with other models (e.g. SAFT variants) for similar systems (e.g. n-decane-water) [22].

3.3.2. Solubility of MEG in COND-1

In the binary system of MEG and condensate, MEG is a self-associating compound whereas hydrocarbons are inert or non-associating. The only binary interaction parameter therefore required is that between MEG and each HC (fraction from C_3 to C_{23}) whereas no combining rules are required.

The CPA correlation for solubility of MEG in COND-1 along with the experimental data are given in Figure 6. The solubility of MEG in condensate is estimated satisfactorily even with zero interaction parameters ($k_{ij} = 0$). The deviation from the experimental data is seen at higher temperatures and the results can be improved by using smaller non-zero interaction parameter ($k_{ij} = 0.01$). In the previous work of Yan et al. [6] an average k_{ij} =0.05 has been used for MEG and HC. Using the interaction parameter of 0.05 between MEG and hydrocarbons, CPA under-estimates the solubility of MEG in COND-1 which may be due to the presence of aromatics in the condensate.

Mutual Solubility of MEG and COND-1

The mutual solubility of MEG and COND-1 using the CPA EoS with k_{ij} used for MEG-HC is shown in Figure 7. Using the interaction parameter (k_{ij}) of 0.01 between MEG and hydrocarbons, promising results are obtained for a solubility of MEG in condensate as shown in Figure 6 but the solubility of condensate in MEG is under-estimated. Using k_{ij} =0 for MEG-HCs, we get a slight over prediction for the solubility of MEG in the HC phase but the polar phase prediction has been improved. The polar phase solubility calculations can further be improved by using a slight negative k_{ij}. It is also observed that the use of a non-zero binary interaction parameter is required when we want simultaneous fitting of solubility of HC in the polar phase and MEG in the HC phase. Similar trends have been observed in the previous work on well defined HC-polar compounds (MEG, water) systems [15]. The % AAD in calculation of mutual solubility for MEG-COND-1 system is given in Table 10 along with the binary interaction parameters used in this study.

3.3.3. Mutual Solubility of MEG, Water and COND-1

In the ternary system of MEG, water and condensate, in addition to self-association, we also have two compounds (MEG, water) which cross-associate. The Elliott combining rule is used for the MEG-water system with k_{ij} =-0.115 taken from the previous work [19].

For the modeling of the mutual solubility of the MEG-water-condensate system, as a first step, a base case has been built as given in Table 11. In the base case only the most crucial interaction parameter between water and MEG is used whereas all the other interaction parameters (including those for MEG-HC and water-HC) are set equal to zero. The results show qualitatively right trends and they are correct in the order of magnitude which seems satisfactory when dealing with the concentration on ppm level in a complex mixture of polar and non polar compounds. The prediction is especially promising when we have higher concentration of MEG in the feed mixture. It is also important to mention that the predictions are as good

as for systems of well defined HC (n-hexane, 2,2,4-trimethylpentane) with MEG and water against recently published data [30, 31].

The modeling results shown in Table 11 can be used as a starting point for the further analysis and optimization of interaction parameters. The binary interaction parameter between MEG-HC and water-HC were kept to zero in the results shown in Table 11 and investigation is then made to see the effect of using non-zero interaction parameters. The final objective is to introduce a generic approach for selection of k_{ij} in the system containing reservoir fluid (oil or gas condensate) and to improve the modeling results. The k_{ij} used for HC-water are given in Table 8 which are obtained using a generalized correlation as function of carbon number [24].

The calculations have been made to investigate the effect of k_{ij} between MEG and HC on the estimation of mutual solubility of HC and polar compounds (MEG, water). The results are given in detail in Table 12 whereas their summary on the basis of percent average absolute deviation (% AAD) is given in Table 13. A comparison with well defined HC, MEG and water system is also presented Table 13.

On the basis of the results given in Tables 12 and 13 and Figure 8 the following conclusions can be drawn:

- Promising results for the estimation of water solubility in HC phase are obtained. Some deviations are also observed for the ternary system, mainly for the MEG solubility in the HC phase and the condensate solubility in polar phase. The solubility of MEG in the HC phase is over estimated whereas of the condensate solubility in the polar phase is under estimated.
- Optimizing the average k_{ij} between MEG-HC is a trade-off between better description of the solubility of MEG in the condensate phase and condensate solubility in polar phase. Lowering the average absolute deviation (AAD) in the modeling results of the solubility of MEG in the condensate phase, increases the AAD for the solubility of condensate in the polar phase as shown in Table 12.
- The under prediction of the solubility of condensate in the polar phase and water in the condensate phase can be explained by solvation but the over prediction of MEG in the condensate is difficult to explain.

The binary interaction parameter (k_{ij}) used in this work and by Yan et al. [6] for all HC-MEG pairs is an average value. The modeling results are expected to improve by using (if available) k_{ij} fitted to binary experimental data for various HC-MEG pair

4. Conclusions

In this work new experimental data for the mutual solubility of the binary (MEG + gas condensate) and the ternary (MEG + water + gas condensate) systems are reported over a range of temperature and at atmospheric pressure. A North sea natural gas condensate with 0.896 % C_3, 2.382 % *i*-C_4, 7.813 % *n*-C_4, 5.502 % *i*-C_5, 7.275 % *n*-C_4, 10.292 % C_6, 16.046 % C_7, 16.632 % C_8, 8.903 % C_9 and 24.254 % C_{10+} is used.

The CPA EoS has been applied to the modeling of the mixture containing natural gas condensate, MEG and water. Satisfactory modeling results are obtained for mutual solubility of MEG and condensate. The prediction is satisfactory with zero interaction parameters between MEG and HC. For the ternary system, the results are qualitatively correct but some deviations are observed. In addition, the modeling results are as good as for systems of well defined hydrocarbons (n-hexane, 2,2,4-trimethylpentane) with MEG and water. The modeling results for MEG-water-condensate system may be improved if the experimental data are available for well defined HC and MEG pairs, fitting k_{ij} for each MEG-HC pair and using them instead of average binary interaction parameters.

List of Symbols

a_0	parameter in the energy term of CPA $\left(bar.L^2 / mol^2\right)$
b	co-volume parameter
c_1	parameter in the energy term of CPA
$g(\rho)$	radial distribution function
k_{ij}	binary interaction parameter in the CPA equation of state
MW	molecular weight
P	pressure
P_c	critical pressure
P_{cm}	CPA "monomer" critical pressure
R	gas constant
SG	specific gravity
SG_0	specific gravity of n-alkanes
T	temperature
T_b	boiling point
T_c	critical temperature
T_{cm}	CPA "monomer" critical temperature
v	molar volume
X_{A_i}	the fraction of A-sites of molecule i that are not bonded with other active sites
x_i	analytical mole fraction of component i
w_i	mass fraction of component i

Greek letters

$\beta^{A_iB_j}$	association volume
$\Delta^{A_iB_j}$	association strength between site A on molecule i and site B on molecule j
$\varepsilon^{A_iB_j}$	association energy
ρ	density
ω	acentric factor
ω_m	CPA "monomer" acentric factor

Subscripts

i	component i
j	component j

List of abbreviations

AAD	average absolute deviation=	$\frac{1}{NP}\sum_{i=1}^{NP}\left\lvert\frac{x_i^{cal.}-x_i^{\exp.}}{x_i^{\exp.}}\right\rvert\times 100$
COND-1	gas condensate 1	
CPA	Cubic-Plus-Association equation of state	
% Dev.	percent deviation =	$\left(\frac{x_i^{cal.}-x_i^{\exp.}}{x_i^{\exp.}}\right)\times 100$
ECR	Elliott combining rule	
EoS	equation of state	
Exp.	experimental	
FID	flame ionization detector	
GC	gas chromatography	
GC1	gas chromatograph 1	
GC2	gas chromatograph 2	
GCs	gas chromatographs	
HC	hydrocarbon	
LLE	liquid-liquid equilibrium	
MEG	monoethylene glycol	
NP	number of points	
SRK	Soave-Redlich-Kwong equation of state	

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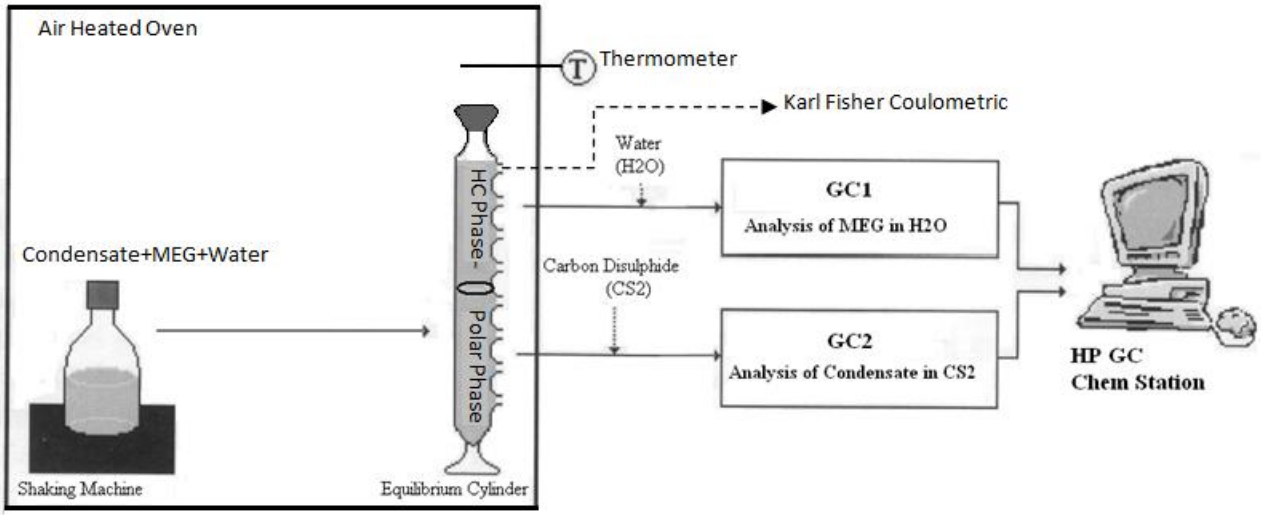

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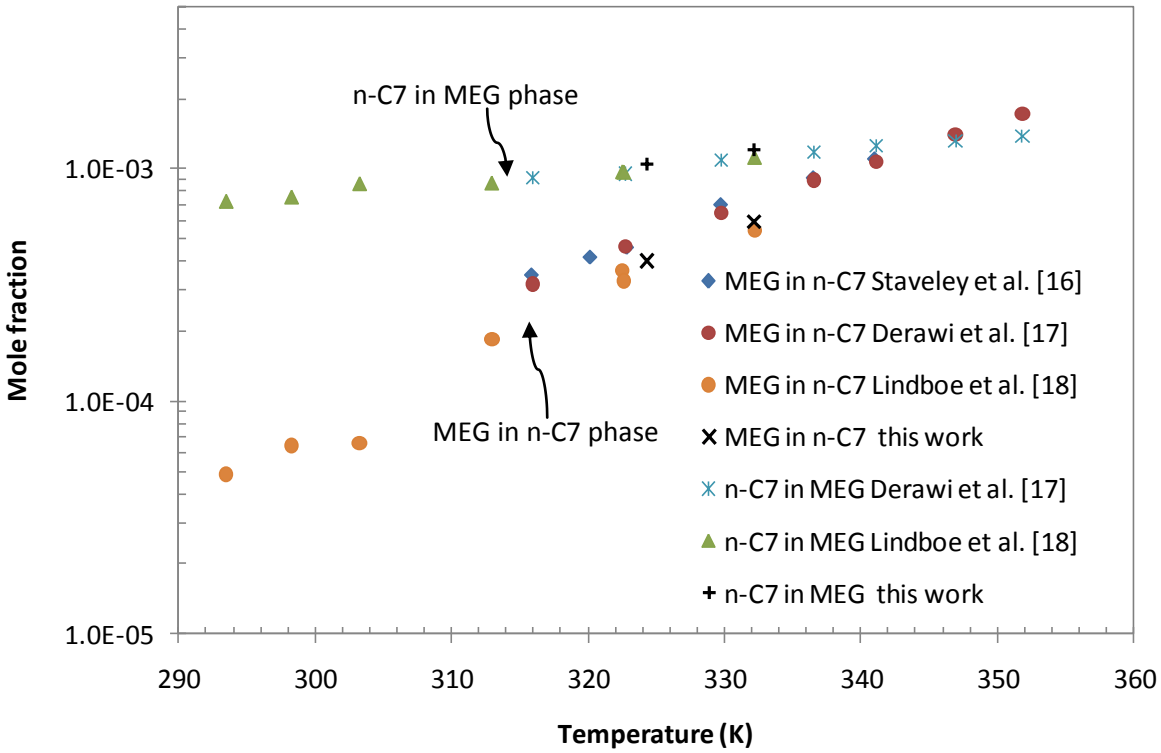
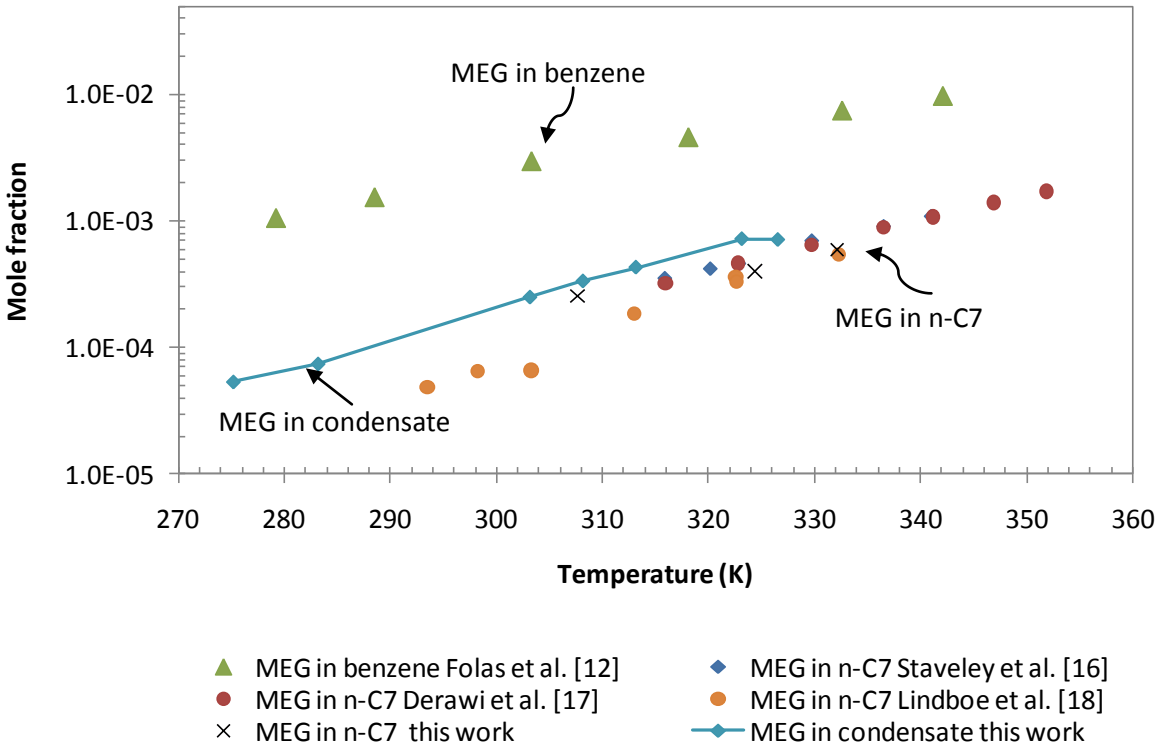


Figure 2. LLE data for n-heptane-MEG and comparison of experimental results from literature.



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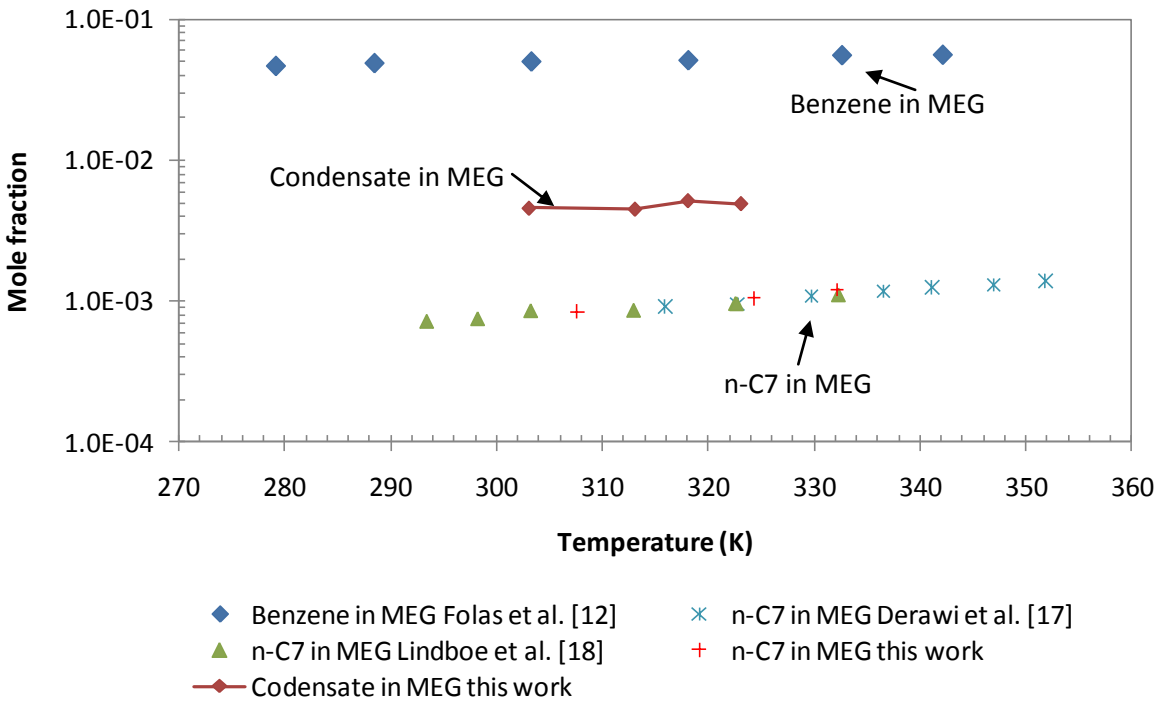

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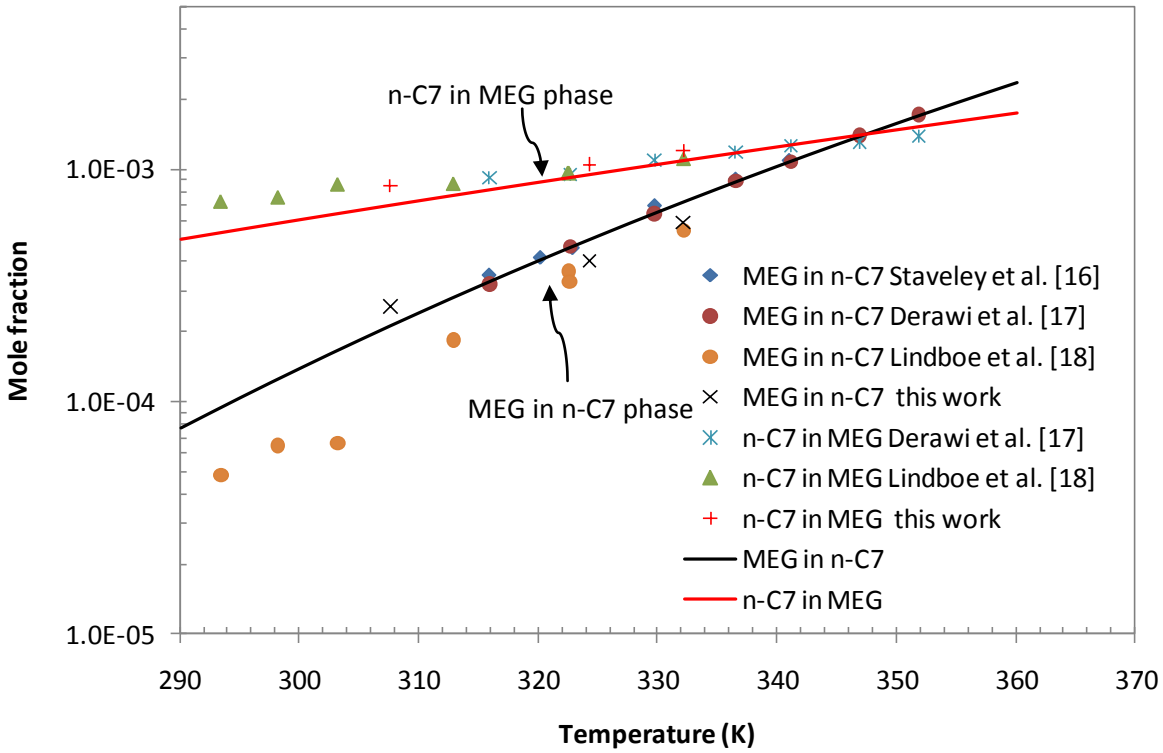

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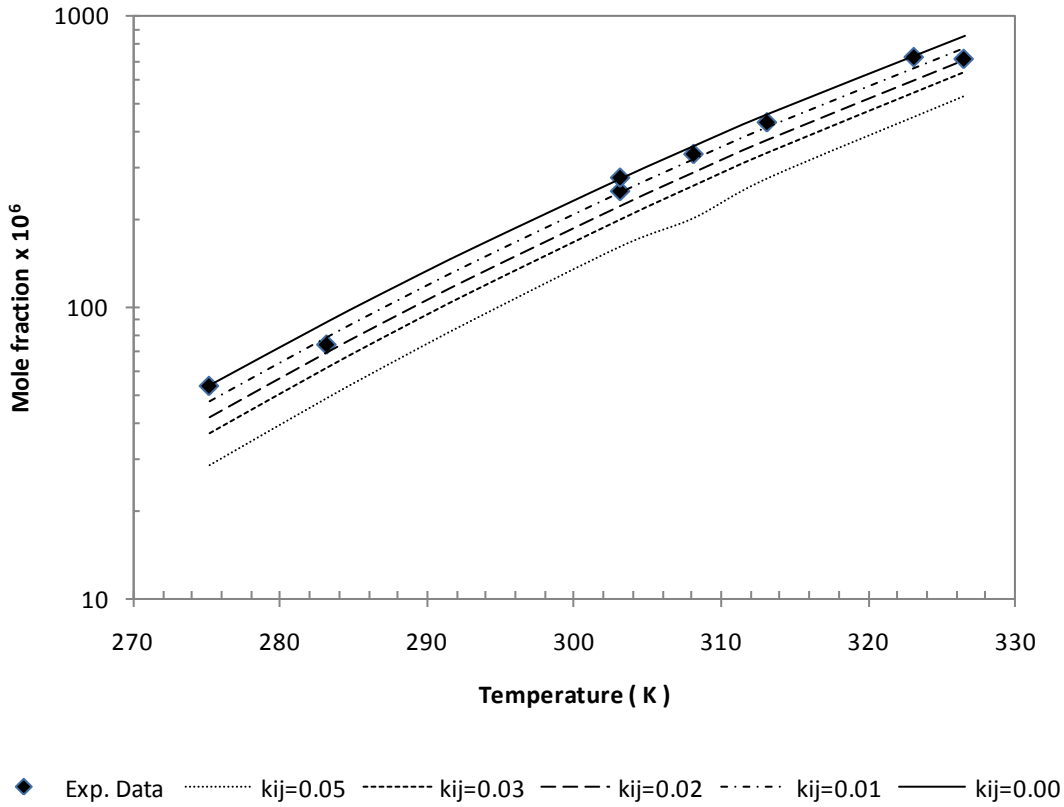


Figure 6. Prediction of the solubility of MEG in COND-1 using the CPA EoS and the effect of using average binary interaction parameter (k_{ij}) between all MEG and HC pairs.

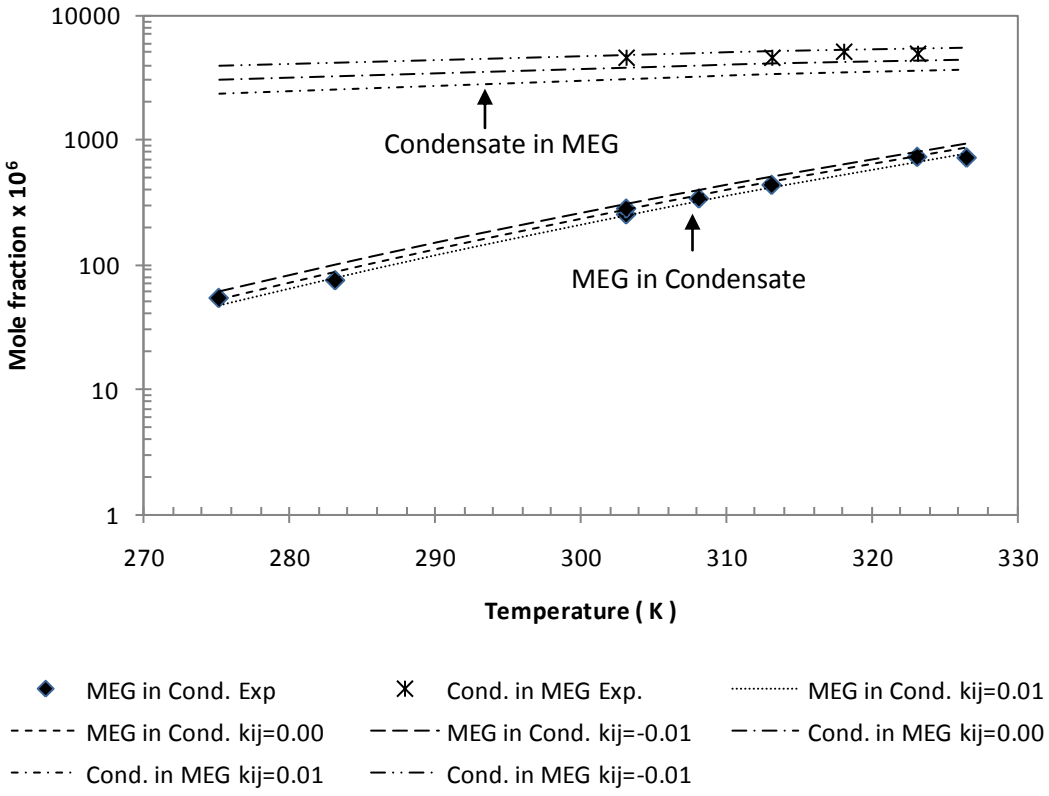
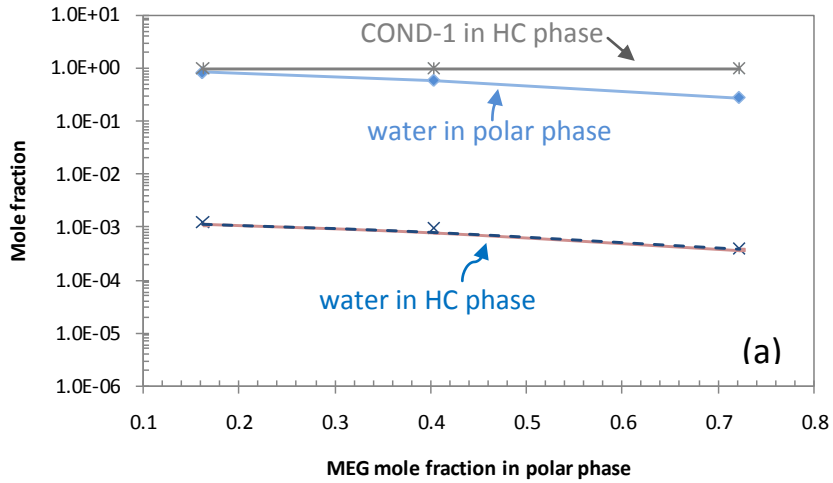


Figure 7. Prediction of the mutual solubility of MEG and COND-1 using the CPA EoS and effect of using average binary interaction parameter (k_{ij}) between all MEG and HC pairs.



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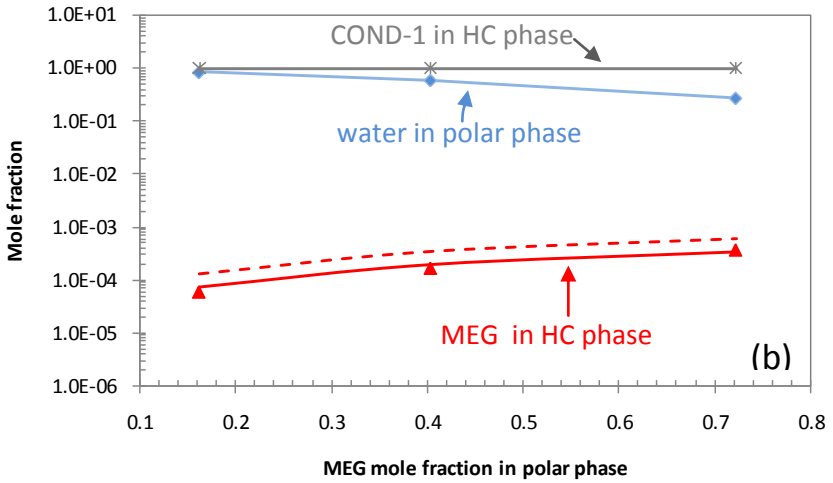

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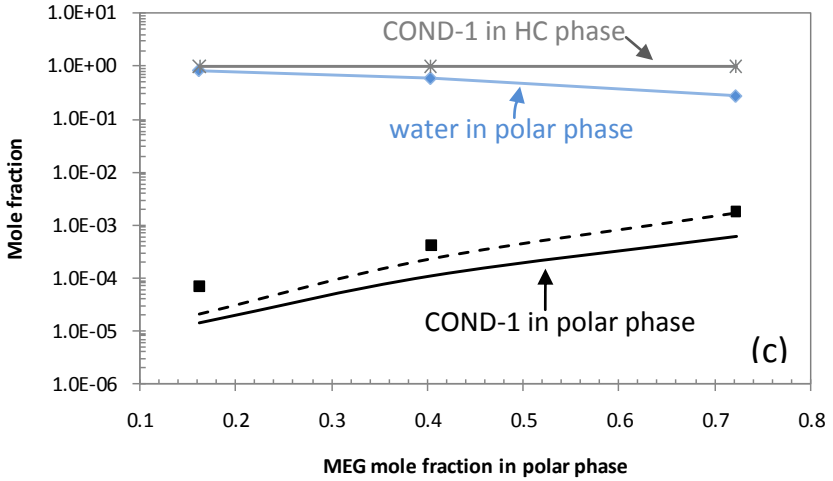

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4 **Figure 8. Mutual solubility of MEG-water and COND-1 at temperature 323.15 K and pressure of 1 atm. (a)**
5 **water in condensate (b) MEG in condensate (c) condensate in polar phase. The points are**
6 **experimental data and the lines are modeling results using CPA. The continuous lines are**

by using average k_{ij} =0.05 for MEG-HC and the dotted lines by using k_{ij} =-0.01 for MEG-HC. The k_{ij} s for MEG-water and HC-Water are the same for the both cases.

List of Tables

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2 **Table 1. Specifications of the chemicals used in this work.**

Chemicals	Specific Purity	Water Contents	Supplier
Ethylene glycol	>99.78%	<0.119%	Acros Organics
Dodecane	>99.99%	<0.001%	MERCK
Carbon disulphide	>99.78%	<0.119%	Acros Organics

3

4

1 **Table 2. Characteristics of gas chromatograph used in this work.**

Characteristic	GC1 (Glycol GC)	GC2 (Condensate GC)
Column Name	CP-Wax 52 CB	HP-PONA
Column Type	Polar Column	Non-polar Column
Column Length (m)	30 m	50 m
Column Internal Dia. (mm)	0.53 mm	0.2 mm
Column film thickness (µm)	1 µm	0.5 µm
Injector	0.2 µl	0.1 µl
Carrier gas	Helium	Helium
Detector type	FID	FID

2
3

Table 3. Composition, molecular weight and density of COND-1.

Component	Mole %	Molecular weight	Density kg/m^3
Methane	0.000		
Ethane	0.004		
Propane	0.896		
iso-Butane	2.382		
n-Butane	7.813		
iso-Pentane	5.502		
n-Pentane	7.275		
C_6	10.292		
C_7	16.046	91.4	736.2
C_8	16.632	103.6	768.6
C_9	8.903	118.5	780.6
C_{10+}	24.254	189.4	846.4
Average molecular weight	----	112.7	----
Overall density	----	----	756.2

Table 4. Measured solubility of MEG in COND-1 for the binary MEG+COND-1 system, expressed as mole ppm at 1 atm.

Temperature (K)	MEG in COND-1 (mole ppm)	COND-1 in MEG (mole ppm)
275.15	53.39	---
283.15	74.06	---
303.15	249.73	4590
308.15	334.99	---
313.15	430.56	4524
318.15	---	5170
323.15	721.82	4937
326.55	711.31	---

Table 5. Equilibrium measurement (in mole fraction) of ternary system of MEG (1), water (2) and COND-1 (3) at temperature 323.15 K and pressure 1 atm.

Feed Mole fraction			**Polar Phase** Mole fraction			**Organic Phase** Mole fraction		
MEG	Water	Cond.	MEG	Water	Cond.	MEG	Water	Cond.
x_1	x_2	x_3	x_1	x_2	$x_3 \times 10^6$	$x_1 \times 10^6$	$x_2 \times 10^6$	$x_3 \times 100$
0.1324	0.6843	0.1833	0.1621	0.8378	69	61	1218	99.87206
0.3041	0.4488	0.2472	0.4037	0.5960	417	172	946	99.88818
0.4992	0.1909	0.3098	0.7222	0.2765	1793	381	402	99.92168

Table 6. CPA pure component parameters used in the calculations.

Components	Reference	Assoc. Scheme	a_0 (L^2bar/mol^2)	b (L/mol)	c_1	T_c (K)	ε (bar L/mol)	$\beta \times 10^3$
MEG	[19]	4C	10.81900	0.051400	0.67440	720.00	197.52	14.1
Water	[20]	4C	1.2277	0.014515	0.67359	647.29	166.55	69.2
n-heptane	[21]	---	29.178	0.125350	0.91370	540.20	---	---

1 **Table 7. Binary interaction parameters for LLE of MEG - HC systems.**

System	Reference	k_{ij}
MEG-methane	[22]	0.134
MEG-hexane	[23]	0.059
MEG-heptane	[23]	0.047
MEG-methylcyclohexane	[23]	0.061

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Table 8. Binary interaction parameters for LLE of water-hydrocarbon systems, based on the generalized expression which is valid from propane up to n-decane: k_{ij} = -0.026.(carbon number)+0.1915 [24].

Hydrocarbon	T range (K)	k_{ij}	% AAD in x_{HC}	% AAD in x_w
Propane	278 - 366	0.1135	35.9	3.4
Butane	310 - 420	0.0875	26.5	11.7
n-pentane	280 - 420	0.0615	28.4	13.4
n-hexane/cyclohexane	280 - 473	0.0422[1]	31.1	---
n-heptane	280 - 420	0.0095	63.3	11.5
n-octane	310 - 550	−0.0165	44.1	9.7
n-nonane	290 - 566	−0.0425[2]	---	---
n-decane	290 - 566	−0.0685	264	8.2
n-C_{10} to n-C_{12}	---	−0.0685[3]		---

[1] average of n-hexane and cyclohexane. [2] using generalized correlation. [3] same as for n-decane

1 **Table 9. Mixture in Table 3 (COND-1) after characterization and lumping.**

Components	Mole %	T_{cm} (K)	P_{cm} (bar)	ω_m
Propane	0.90	369.8	42.5	0.152
i-Butane	2.38	408.1	36.5	0.176
n-Butane	7.81	425.2	38.0	0.193
i-Pentane	5.50	460.4	33.8	0.227
n-Pentane	7.28	469.6	33.7	0.251
C_6	10.29	507.4	29.7	0.296
C_7	16.05	527.8	33.9	0.454
C_8	16.63	551.6	31.3	0.490
C_9	8.90	573.9	27.3	0.533
C_{10}	5.04	597.9	24.2	0.582
C_{11}	3.99	615.9	22.6	0.621
C_{12}	3.16	632.8	21.3	0.659
C_{13}	2.51	648.7	20.3	0.696
C_{14}	1.99	663.8	19.5	0.732
C_{15}	2.82	684.6	18.6	0.784
C_{17}- C_{18}	1.77	711.3	17.6	0.852
C_{19}- C_{22}	1.81	746.0	16.8	0.942
C_{23+}	1.18	824.1	15.8	1.127

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Table 10. CPA modeling of MEG-COND-1 system and the effect of k_{ij} on mutual solubility of MEG and COND-1.

k_{ij} of MEG-HC	% AAD (MEG in Condensate)	% ADD (Condensate in MEG)
0.05	36	>29
0.03	20	>29
0.02	11	>29
0.01	1	29
0.00	11	12
-0.01	24	9

Table 11. Equilibrium measurement and modeling of ternary system MEG (1)-water (2)-COND-1 (3) at temperature 323.15 K and pressure 1 atm. The k_{ij} for MEG-water=-0.115 is used and all the other k_{ij} between MEG-HC and water-HC are set equal to zero.

Component	Feed (mole fraction)	Polar Phase (mole ppm)			Hydrocarbon Phase (mole ppm)		
		Exp.	Cal.	% Dev.	Exp.	Cal.	% Dev.
MEG	0.1324	---	---	---	61	117	*92*
Water	0.6843	---	---	---	1218	1049	*-14*
Cond.	0.1833	69	37	*-46*	--	---	---
MEG	0.3041	---	---	---	172	313	*82*
Water	0.4488	---	---	---	946	730	*-23*
Cond.	0.2472	417	272	*-35*	--	---	---
MEG	0.4992	---	---	---	381	547	*44*
Water	0.1909	---	---	---	402	349	*-13*
Cond.	0.3098	1793	1575	*-12*	--	---	---

Table 12. CPA modeling of MEG-water-COND-1 system and investigation of the effect of binary interaction parameters (k_{ij}) on the prediction of mutual solubility of MEG, COND-1 and water.

Components	Feed Compositions	Phase and Results	Interaction parameters (k_{ij})											
			MEG-HC = 0.0 MEG-Water = -0.115 Water-HC = Table 8			MEG-HC = -0.01 MEG-Water = -0.115 Water-HC = Table 8			MEG-HC=0.01 MEG-Water = -0.115 Water-HC = Table 8			MEG-HC=0.05 MEG-Water = -0.115 Water-HC = Table 8		
			Modelling Results											
			HC in Polar Phase	*MEG in HC Phase*	*H_2O in HC Phase*	*HC in Polar Phase*	*MEG in HC Phase*	*H_2O in HC Phase*	*HC in Polar Phase*	*MEG in HC Phase*	*H_2O in HC Phase*	*HC in Polar Phase*	*MEG in HC Phase*	*H_2O in HC Phase*
MEG	0.1324	Exp.	69	61	1218	69	61	1218	69	61	1218	69	61	1218
Water	0.6843	CPA	20	118	1116	21	129	1117	19	107	1116	14	73	1113
Cond.	0.1833	%Dev.	-71	+93	-8	-70	+111	-8	-72	+75	-8	-80	+20	-9
MEG	0.3041	Exp	417	172	946	417	172	946	417	172	946	417	172	946
Water	0.4488	CPA	205	313	775	234	345	777	181	285	774	109	194	770
Cond.	0.2472	%Dev.	-51	+82	-18	-44	+101	-18	-57	+66	-18	-74	+13	-19
MEG	0.4992	Exp.	1793	381	402	1793	381	402	1793	381	402	1793	381	402
Water	0.1909	CPA	1452	548	369	1736	605	371	1218	497	368	614	337	364
Cond.	0.3098	%Dev.	-19	+44	-8	-3	+59	-8	-32	+30	-8	-66	+12	-9
		%AAD	**47**	**73**	**12**	**39**	**90**	**11**	**54**	**57**	**12**	**73**	**15**	**12**

Table 13. CPA modeling of MEG-water-COND-1 system and summary of the results (in term of % AAD) for the effect of k_{ij} on results of the mutual solubility of MEG, water and COND-1 using k_{ij} for MEG-water=-0.115.

% AAD			k_{ij}	
HC in Polar Phase	MEG in HC	H_2O in HC	MEG-HC	Water-HC
73	15	12	0.05	Table 8
54	57	12	0.01	Table 8
47	73	12	0.00	Table 8
39	90	11	-0.01	Table 8
31	72	17	0.00	0.00
% AAD for Well defined system of MEG-water-n-hexane [31]				
44	42	44	0.059	0.0355
% AAD for system of MEG-water-2,2,4 TM-C_5 [31]				
82	83	43	-0.00028	-0.0687